Theor Chem Acc (2007) 117: 163–165
DOI 10.1007/s00214-006-0158-5

REGULAR ARTICLE

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Initial anticrossing between Stark manifold *n* and *n*+1 in Na

Received: 20 March 2006 / Accepted: 7 June 2006 / Published online: 3 August 2006

Abstract We present the theoretical results for the positions and widths of the initial anticrossing between Stark manifold n and $n+1$ in sodium, obtained by using the method of diagonalization in which zero-field wave functions are chosen from a kind of atomic potential model. These results can provide the quantitative information for understanding the microwave ionization process, whose rate-limiting step is probably the n to $n+1$ transition performed at the first crossing between the outermost states of these two manifolds.

Keywords Stark effect · Nonhydrogen atoms · Atomic potential model · Rydberg state · Anticrossing

1 Introduction

The research about the level anti-crossings of a Rydberg atom in a static field is of interest in both atomic theory and experiment [1–7]. The level crossing and anticrossing spectroscopy has been widely used to measure physical quantities of atomic Rydberg states. The anti-crossings of Stark levels also play a significant role in static field ionization [8] and microwave field ionization [9]. Theoretical calculation of anticrossings can provide useful information for the above experiments. Since the positions and widths of anti-crossing have a sensitive dependence on the wave functions chosen, this kind of calculation can be used as a stringent approach to test the accuracy of approximate wave functions and Stark structure calculations [3,9].

Concerning microwave field ionization, for a given microwave frequency and a given initial quantum number n there is a critical microwave field strength or threshold f above which microwave ionization begin. The study of the relation between the threshold f and the initial quantum number n is of interest. For hydrogen atoms, the threshold f scales as $1/n^4$. It is a rather surprising result that the observed microwave threshold fields of Pillet et al. [10,11] for the sodium s and d states with $|m| = 0$ and 1 are close to $f = 1/3n^5$. The significance of the field $f = 1/3n^5$ is that at this field the Stark manifolds of n and $n+1$ overlap based on a qualitative analysis [12,13]. On account of this point, Pillet et al. [10, 11] qualitatively explained ionization at $f = 1/3n^5$ in the following way.

Consider the ionization of a Rydberg sodium atom which initially lies in an $n = 20$ level. In the microwave field the atoms are mixed among the $n = 20$ Stark states, and the field is strong enough, $\approx 1/3n^5$, that the highest energy $n = 20$ state reaches the avoided crossing with the lowest $n = 21$ state, a Landau–Zener transition [8] can occur at the avoided crossing, as shown by Fig. 1 of the paper of Pillet et al. [11]. After performing the $n = 20 \rightarrow n = 21$ transition the atom makes further transitions to higher n states, culminating in field ionization at the classical ionization limit. Since the overlap of the Stark manifolds of higher n states occurs at progressively lower fields, the initial $n = 20 \rightarrow n = 21$ transition is the rate-limiting step, leading to the observed $f = 1/3n^5$ threshold field.

As shown by Pillet et al. [11], the ionization threshold fields for the sodium d states with $|m| = 2$ lie near the $\sim 1/9n^4$ line which is what we would expect for such hydrogenic states. Since *nd* states and all higher-*l* states have small quantum defects, the anticrossings of the $|m| = 2$ states at the intersections of the n and $n+1$ Stark manifolds are very small, approximately corresponding to the hydrogenic situation. Since such crossings can be traversed in a diabatic fashion even with relative slowly rising fields, the Landau–Zener transitions should not occur for the case of $|m| = 2$.

Based on the above interpretation to the microwave ionization, a detailed quantitative information about positions and sizes for the initial anticrossing between Stark manifold n and $n+1$ in Na can definitely provide insight into understanding the microwave ionization process.

Using the wave function derived from a kind of potential model [14] as a basis, we have calculated the locations and widths of the level anti-crossings for Rydberg K, Rb, and Cs in static electric fields by means of diagonalization,

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and obtained results in good agreement with the experimental ones [15–20]. These results have shown the effectiveness of using the potential model to calculate the avoided crossings of alkaline atoms in a static electric field. Therefore it is of great interest to calculate the first anticrossing between levels of different terms in Na by means of the potential model. We will present in this paper the results for the positions and widths of avoided crossings in sodium when a static electric field applies.

2 Methods and Results

The Hamiltonian for an alkaline metal atom subject to a static field F along the z axis is as followings (in atomic unit):

$$H = -\frac{1}{2}\nabla^2 + V(r) + Fz \tag{1}$$

In investigating the avoided crossing, the energy difference of the two relevant energy levels is taken as the function of the electric field. The minimal value of this function is at the point where location of the anticrossing is defined, and the width of anticrossing is defined as this minimal value.

In order to obtain positions and widths of avoided crossings of Stark states of sodium, we need to know the eigenvalues of the Hamiltonian (1). We tackle this eigenvalue problem with the diagonalization method, in which the bases are chosen from zero field wave functions deduced from a kind of analytic potential model [14].

Considering the penetration and polarization effect, the core potential of an alkali-metal atom is assumed to take the form [14]

$$V(r) = -\frac{1}{r}\left(1 + \frac{\beta'}{(r+\gamma')^2} + \frac{\kappa'}{(r+\xi')^2}\right) \tag{2}$$

The wavefunction in a zero field has the form $\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\varphi)$, where $Y_{lm}(\theta,\varphi)$ is a spherical harmonic. $R_{nl}(r)$ has an analytic form

$$R_{nl}(r) = N\exp(-\rho/2)\rho^s(\rho+\gamma)^t(\rho+\xi)^u\sum_{v=0} a_v\rho^v,$$
$$a_0 = 1, \tag{3}$$

in which,

$$\rho = \alpha r, \quad \gamma = \alpha\gamma', \quad \xi = \alpha\xi', \quad \alpha = 2/n^*,$$
$$n^* = n - \delta_{nl}, \tag{4}$$

where $s, t, u, a_v, \beta', \gamma', \xi', \kappa'$, which depend on n and l, are the parameters to be determined; and δ_{nl} is the quantum defect. Substituting $R_{nl}(r)$ and $V(r)$ into the radial Schrodinger equation, and then equating the coefficients of the corresponding terms of ρ and considering the asymptotic behavior and the standard condition for a radial wavefunction, we obtain the nonlinear algebraic equations of the above parameters. Solving them by using Broyden's method (quasi-Newton method), we get $s, t, u, a_v, \beta', \gamma', \xi', \kappa'$, and then $R_{nl}(r)$ and $V(r)$ in their analytic forms, where the sole input parameter δ_{nl} can be determined by experiments. For a detailed derivation see [14]. The radial wavefunction $R_{nl}(r)$ depends on l in three ways. Firstly, the parameter s is equal to l. And $R_{nl}(r)$ behaves as r^l for small r. Finally, other parameters in $R_{nl}(r)$ depend on l via quantum defect δ_{nl}. This radial wavefunction has the correct number of nodes, does not diverge in the origin of coordinates; moreover, it has the form close to that of H–F–S wavefunction. Although such radial wave functions are not orthogonal due to the state-dependence of $V(r)$, the non-orthogonality has been shown to be negligible especially in the case of higher n states mainly concerned in this paper [14].

Using the above wavefunctions as a basis, the matrix of Hamiltonian equation (1) has the following form

$$H_{nlm,n'l'm} = \frac{-\delta_{nlm,n'l'm}}{2(n-\delta_{nl})^2} + F\langle r\rangle_{nl,n'l'}\langle\cos(\theta)\rangle_{lm,l'm} \tag{5}$$

where $\delta_{nlm,n'l'm}$ is a δ-function. $\langle r\rangle_{nl,n'l'} = \langle R_{nl}|r|R_{n'l'}\rangle$ in $H_{nlm,n'l'm}$ is calculated by numerical integration. Because the off-diagonal matrix element of r, $\langle r\rangle_{nl,n'l'} = \langle R_{nl}|r|R_{n'l'}\rangle$, decreases rapidly as the energy difference increases between corresponding two states, the basis is chosen only in the vicinity of the studied state. Thus, the basis from the potential model has a good convergence behavior.

In view of the fact that our method has been successfully used to calculate positions and widths of K, Rb and Cs, to ensure the accuracy of theoretical results, the only point that we should take care of is that the quantum defects of sodium should have a high accuracy. The values of quantum defect employed in our calculation are obtained by highly accurate experimental energies for low n states and the extended Rize formula [21].

We calculate the locations and sizes of the first anti-crossing between levels of different terms in Na for the case of $|m| = 0 - 2$ and $n = 15 - 35$. The basis set is chosen from the zero-field potential model wavefunctions of $n-4$ to $n+7$ manifolds. This choice of basis set has warranted the convergence of the related positions and widths. The results are presented in Tables 1, 2.

As stated in the introduction of this paper, one of the important points that leads to the explanation of the multistep process for microwave ionization is that the initial anticrossing between Stark manifold n and $n+1$ occurs at $\approx 1/3n^5$, which is obtained from a qualitative analysis [12,13]. In order to compare the calculated locations of anticrossing with the $1/3n^5$ scaling law, the field positions of $1/3n^5$ in atomic unit or $1.71\times10^9 n^{-5}$ in unit of V/cm are also listed in Table 1. From Table 1, we can see that basically all field positions of the first anticrossing between Stark manifold n and $n+1$ follow the $1/3n^5$ scaling law. But the positions for $|m| = 0$ and 1 is slightly lower than the ones from $1/3n^5$ scaling law and the positions for $|m| = 2$ are slightly higher. According to a qualitative analysis, the Stark shift of the extreme $|m| = 1$ levels is lower than the extreme $|m| = 0$ level by the factor $1 - 1/n$. Therefore the n and $n+1$ $|m| = 1$ Stark manifolds intersect at a field $1 + 1/n$ higher than the field of the $|m| = 0$ intersection [11]. Our results quantitatively

Table 1 The calculated locations of the first anticrossing between levels of different terms in Na for the case of $|m| = 0-2$. The position from the scaling law $1/3n^5$ in atomic unit or $1.71 \times 10^9 n^{-5}$ in unit of V/cm are also listed

n	$\|m\| = 0$ Position (V/cm)	$\|m\| = 1$ Position (V/cm)	$\|m\| = 2$ Position (V/cm)	$1/3n^5$ Position (V/cm)
15	2163	2194	2365	2251
16	1569	1592	1707	1631
17	1160	1177	1256	1204
18	873.0	885.6	941.4	905.0
19	667.0	676.6	716.7	690.6
20	516.8	524.1	553.4	534.4
21	405.4	411.0	432.7	418.7
22	321.6	326.0	342.4	331.8
23	257.8	261.2	273.7	265.7
24	208.5	211.3	220.9	214.8
25	170.2	172.4	179.9	175.1
26	140.0	141.8	147.7	143.9
27	116.0	117.5	122.2	119.2
28	96.81	98.00	101.8	99.36
29	81.29	82.27	85.32	83.37
30	68.66	69.47	71.96	70.37
31	58.32	58.99	61.03	59.73
32	49.79	50.35	52.03	50.96
33	42.71	43.19	44.59	43.69
34	36.81	37.22	38.38	37.64
35	31.86	32.21	33.18	32.56

Table 2 The calculated sizes of the first anticrossing between levels of different terms in Na for the case of $|m| = 0-2$

n	$\|m\| = 0$ Width (1/cm)	$\|m\| = 1$ Width (1/cm)	$m\| = 2$ Width (1/cm)
15	1.211	5.621-1	1.075-2
16	9.016-1	4.120-1	7.235-3
17	6.836-1	3.072-1	4.981-3
18	5.268-1	2.329-1	3.503-3
19	4.120-1	1.791-1	2.514-3
20	3.263-1	1.395-1	1.826-3
21	2.615-1	1.100-1	1.351-3
22	2.118-1	8.764-2	1.013-3
23	1.732-1	7.053-2	7.692-4
24	1.429-1	5.726-2	5.911-4
25	1.188-1	4.688-2	4.597-4
26	9.956-2	3.868-2	3.617-4
27	8.401-2	3.221-2	2.851-4
28	7.130-2	2.689-2	2.323-4
29	6.088-2	2.623-2	1.833-4
30	5.227-2	1.915-2	1.486-4
31	4.511-2	1.630-2	1.213-4
32	3.912-2	1.395-2	9.968-5
33	3.407-2	1.198-2	8.243-5
34	2.980-2	1.036-2	6.864-5
35	2.617-2	8.897-3	5.741-5

confirm this point since the calculated positions for $|m| = 0$ is slightly lower than the ones for $|m| = 1$.

The anticrossing widths are shown Table 2 for the case $|m| = 0-2$. As mentioned in the first section of this paper, the widths have an important influence on determining if Landau–Zener transition occurs at anticrossing position. From Table 2, we can see that widths for the case of $|m| = 2$ are much smaller than ones in $|m| = 0$ and 1. This quantitatively explains why the Landau–Zener transition is unable to occur at the anticrossing position for the case of $|m| = 2$.

The scaling law for anticrossing is helpful in both providing insight into understanding ionization mechanism and predicting quantitative features for future experiments. Here, we present the scaling law of the field positions, which is obtained by using least-squares fits to our theoretical positions. The locations of initial anticrossing between Stark manifold n and $n+1$ in Na are given by

$$|m| = 0, \quad f = 1.65 \times 10^9 n^{-5} (V/cm) \tag{6}$$

$$|m| = 1, \quad f = 1.67 \times 10^9 n^{-5} (V/cm) \tag{7}$$

$$|m| = 2, \quad f = 1.79 \times 10^9 n^{-5} (V/cm) \tag{8}$$

Summarizing, we present in this paper the theoretical results for the positions and widths of the initial anticrossing between Stark manifold n and $n+1$ in sodium, which are obtained by using the method of diagonlization in which zero-field wave functions are chosen from a potential model. These results can provide the quantitative information for understanding microwave ionization process, whose rate-limiting step is probably the n to $n+1$ transition performed at the first crossing between the outermost states of these two manifolds.

Acknowledgements The project is sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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